Hydrothermal Liquefaction and Product Characterization of Barley Straw in Sub- and Super Critical Water

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Table 2. Elemental analysis of bio-oil

Hydrothermal Liquefaction and Product Characterization of Barley Straw in Sub- and Supercritical Water

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INTRODUCTION

With the rapid development of global economy and the continuous increase of the population, the demand and consumption of energy has been increasing. Biofuels are **renewable liquid transportation fuels**, which can be obtained by hydrothermal liquefaction (HTL).

HTL is a **wet thermal conversion process** that performed under relatively **mild reaction conditions** (temperature less than 400 °C, pressure between 10 and 25 MPa), often in the presence of catalysts and sometimes with reducing gases such as CO and H_2.

Energy-consuming drying process is avoided in this process. In addition, **better quality bio-oil with low oxygen content and consequently a higher heating value** can be produced under carefully control of operation conditions.

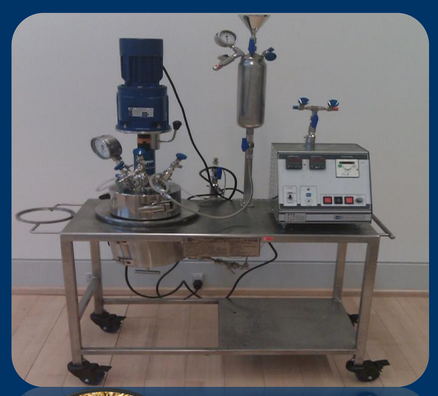
OBJECTIVE

- **Investigate the effect of final reaction temperature** on product distribution and yield.
- **Characterize HTL bio-oils and solid residues** obtained from different temperatures in order to have a better understanding of the reaction process.
- **Evaluate the elemental content and distribution and energy recovery** in these products.

MATERIALS AND METHODS

The Characteristic of Barley Straw

C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	H/C	O/C	Water Content (wt%)	HHV (MJ/kg)
44.66	6.34	0.46	0.57	47.97	1.70	0.81	6.21	17.38



Reaction conditions:

1L batch reactor

Temperature: 280-400 °C

Catalyst: 10wt% K_2CO_3 based on the straw

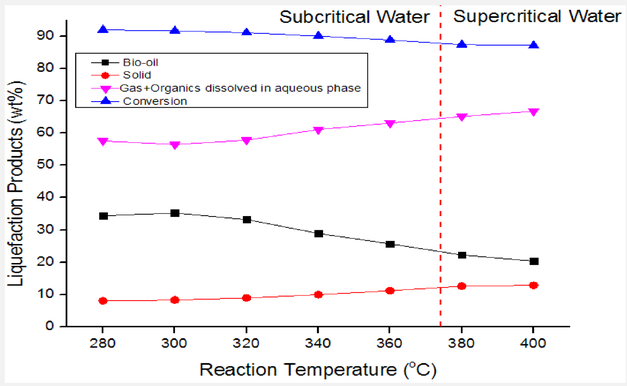
Retention time: 15min

STRAW

- Bio-oil
- Aqueous Phase
- Solid Residues
- Gas

RESULTS AND DISCUSSION

Product Distribution and Biomass Conversion



Bio-oil yield increased slightly from 280 °C to 300 °C and **peaked at 300 °C (35.24 wt%)** and then declined as the temperature increased further, while the yield of solid residues showed the opposite trend.

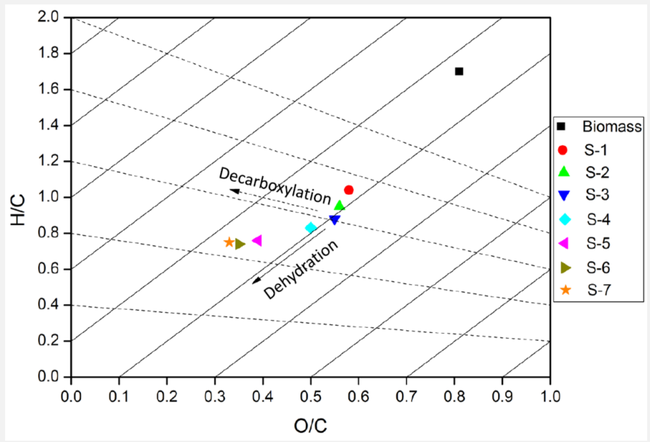
High conversion of straw between 87.13 and 91.97 wt% could be reached under tested conditions.

Elemental Analysis of Bio-oil

Sample	T (°C)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt)	H/C	O/C	HHV (MJ/kg)
O-1	280	67.03	7.36	0.77	0.54	24.30	1.32	0.27	26.75
O-2	300	67.89	7.62	0.75	0.56	23.18	1.35	0.26	27.29
O-3	320	68.77	7.65	0.80	0.65	22.13	1.33	0.24	28.63
O-4	340	70.84	7.52	0.71	0.54	20.39	1.27	0.21	30.47
O-5	360	72.81	7.73	0.78	0.54	18.14	1.27	0.19	32.16
O-6	380	75.23	7.46	0.78	0.49	16.05	1.19	0.16	34.58
O-7	400	77.22	7.36	0.79	0.56	14.07	1.14	0.14	35.48
Petroleum	-	83-87	10-14	0.1-1.0	0.1-8	0.1-3	-	-	42.7

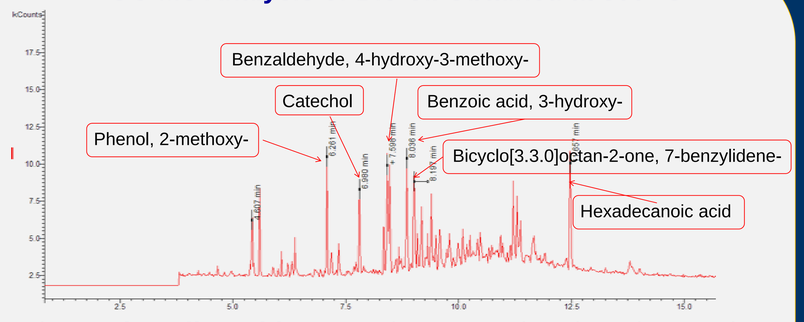
The **C content of bio-oil generally increased** with the increase in temperature, while **a decrease in O content** was observed.

Van Krevelen Diagram of Barley Straw and Solids



Data suggested that dehydration and decarboxylation occurred in this process, and **dehydration was the dominant reaction**.

GC-MS Analysis of Bio-oil Obtained at 300 °C



The **carboxylic acids** were the most abundant (30.82%), followed by **phenolic compounds** and its derivatives (19.18%), **ketones** (16.12%) and **aldehydes** (9.11%).

Elemental Recovery and Energy Recovery

Sample	Carbon recovery (%)	Hydrogen recovery (%)	Energy densification	Energy recovery (%)
O-1	51.59	39.90	1.54	52.90
O-2	53.57	42.35	1.57	55.33
O-3	51.20	40.12	1.65	54.77
O-4	45.90	34.33	1.75	50.74
O-5	41.92	31.35	1.85	47.57
O-6	37.48	26.18	1.99	44.27
O-7	35.19	23.62	2.04	41.54
S-1	9.50	5.80	0.99	7.93
S-2	10.05	5.58	0.99	8.24
S-3	10.88	5.61	0.98	8.74
S-4	12.62	6.17	1.04	10.31
S-5	15.58	6.91	1.20	13.43
S-6	18.27	7.97	1.29	16.20
S-7	18.95	8.30	1.32	17.00

CONCLUSIONS

HTL of barley straw is **an effective method** to produce liquid fuels, which has the potential to be used as renewable fuels and a source of chemical materials.

Both yield and characteristics of products (bio-oil and solid residues) were strongly **dependent on final reaction temperature**.

A **maximum bio-oil yield** of 35.25 wt% of dry feedstock with **75.51 % of carbon plus hydrogen content**, **representing 55.33 % of the energy recovery** of the feedstock was obtained at temperature of 300 °C.

FUTURE WORK

Carry out high resolution **parametric study** (heating rate, amount and type of catalyst, reaction time, DM content) to study effect on the product yield and properties.

FLEXIFUEL
Sino-Danish Collaboration
Danish Council for Strategic Research

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